Materials for cryogenic storage of hydrogen and natural gas

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Materials for Cryogenic Storage of Hydrogen and Natural Gas

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Abstract In the present project a limited series of experiments have been carried out, aiming at describing the properties of a number of selected plastic composite materials in relation to their utilisation as construction materials for liquid gas containers. The experiments have been concerned with the measurement of gas diffusion through the composite materials and with the mechanical properties at low temperatures.

Gas diffusion into the materials was measured by gravimetry in an ultra-microbalance. No uptake of gas was found at 77 K for any of the measured materials or materials combinations. For the majority of materials no uptake could be detected even at room temperature. In one case, PEEK, an uptake was measured at room temperature, but the rate was so low that it could be concluded not to represent a hazard in practice.

The mechanical properties of 7 composite samples were measured by tensile testing and simultaneous recording of the accumulated acoustic emission caused by crack formation. In one measurement out of 7 the acoustic emission indicated crack formation at relatively low stresses (i.e. below 150 MPa. The rest of the samples only showed negligible acoustic emission up to 150 MPa, which is considered to be sufficient for application of the material in a liquid gas container.

The work done in the project indicates that plastic composites are suitable for application in low temperature gas containers. More exhaustive measurements of hazard-related physical and chemical materials properties are needed though, before a pilot container can actually be designed. In particular the reaction of the materials to long-term gas exposure needs to be characterised, and also more dedicated diffusion experiments should be carried out, recommendably done in a diffusion cell, where the material to be tested can be suspended as a diaphragm separating a pressure difference.

Experiments should also be designed to test the mechanical properties of the composite materials at the actual temperature of liquid hydrogen and natural gas. The boiling point of hydrogen at atmospheric pressure is about 20 K, which is 57 K below the test temperature applied in this project.

Finally it is recommended to study the reaction of the materials to continued temperature cycling between ambient temperature and the low service temperature. This study should incorporate the aspects of fatigue as well as temperature chock resistance.

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Contents

Preface

The present report describes the results of a series of experiments carried out at Risø National Laboratories to characterise the behaviour of plastic composite materials at low temperatures. The experiments were one part of a project supported by the Danish Energy Agency under the Danish Energy Research Plan EFP-94 (project no. 1443/94-0003). Another part of the project was a literature survey on the same topic. This part of the project has been described in the report (in Danish) "Materialer til kryogen lagring af naturgas og brint", Risø-R-904(DA), published by June 1996.

The aim of the project was to illustrate the potential for application of plastic composites in gas storage and transportation at very low temperatures and to descibe the extent, to which this problem has already been adressed by workers in other laboratories.

The author would like to acknowledge the valuable assistance to the project of J. Kjøller, B. larsen, F. Adrian, J. Larsen, Aa. Lystrup, and H. Toftegaard, all of the Materials Department, Risø National Laboratory.

1 Literature Search

The results of the literature search are described in details in a separate report (Risø-R-904, in Danish). In the present report only the conclusions from the literature search are rendered:

The literature search showed, that the technical interest in plastic composites for gas storage is particularly concentrated within space industry research and development, where the application will be in containers for storage of liquid hydrogen for propulsion in rockets. In this type of application, the weight of the containers is obviously decisive.

However, alternative potential applications reach much farther, also within industrial areas of interest to Danish industry including domestic utilisation. A good example is a container for transport of liquid propellant, which are gaseous at standard pressure and temperature. In a time horizon of 10 - 20 years, especially transport of liquid natural gas can be expected to achieve a markedly increasing significance and in the future beyond that transport of liquid hydrogen may well become important in Danish energy distribution (see e.g. Morthorst et al. "Brint som energibærer" (Hydrogen as an Energy Carrier, in Danish), Risø-R-675(DA)). In this context "transport of gas" also covers the transport of fuel connected with daily person and goods transport by car or truck. Both from an environmental and from an economic point of view there is a strong interest in increased utilisation of natural gas for this kind of transport. The total weight of the vehicles will be a key factor in such applications and favour the use plastic-based materials for fuel tanks.

The materials, which have been the objects for the investigations done until now, have almost exclusively been within groups of materials that are already well known from structural applications at normal temperatures. Many early works were concentrated about glass fibre reinforced plastics, but later on also carbon fibres in matrix materials like PEEK and PTFE have been studied. These materials are known also from Danish research and development, where an ongoing project focuses on new production methods for parts in advanced thermoplastic composite materials.

Many workers have also been interested in the isolation materials necessary to maintain low temperatures used in cryogen storage, also in conjunction with fibre reinforced plastics as a construction material. The possibility of integrating the isolation material and the fibre reinforcement in one material may be an interesting possibility, which has been studied in paper 21 mentioned in the report of the literature search.

The application of a liner, a thin layer of diffusion tight material, on one side of the plastic material used as construction material in a tank wall, is treated in several publications. Especially titanium and aluminium have been considered. The data for diffusion of hydrogen through plastic composites found in the present literature search do not indicate that a liner should be necessary. At room temperature very low diffusion speeds have been measured through glass fibre reinforced epoxy and at the considerably lower service temperatures of a cryogen storage tank, the diffusion speed must be expected to be significantly lower as well.

On the background of the literature search a need is recognised for further investigations and studies of the potential plastic composite materials, in particular regarding safety aspects in relation to their application in cryogenic gas storage. This is true for properties like permeability to the stored gas, mechanical properties at low temperatures and resistance to thermo-chock in consequence of repeated temperature changes during service. Materials properties after ripening is another important point, that should be further investigated.

The present project, partly financed by the Danish ministry of Energy, has incorporated a limited number of experiments with the purpose to illustrate some of the mentioned properties for a number of candidate plastic composite materials. The results of these experiments are reported in the present report.

2 Materials Selection

The Materials Department of Risø National Laboratory has been engaged in activities involving fibre reinforced plastic composites intended for structural applications for many years. The work started around 1975 aiming at strong and light materials for rotor blades for wind mills and has developed ever since within numerous application areas. The work was initially based mainly on thermo-curing plastic materials, but during the latest decennium, a growing focus on the environment and occupational hazards has led to a shift in the Materials Department, so that a majority of projects are today centred around the thermo-plastic types of materials. None of these ongoing activities are concerned with low temperature applications of the composite materials, i.e. temperatures far below the freezing point of water.

The materials selection in the present project was done on the background of the present experiences in the Department and the results of the literature mentioned earlier. The selected materials were:

1. Glass fibres in polyester
2. Glass fibres in polyethylene
3. Glass fibres in epoxy
4. Carbon fibres in epoxy
5. Carbon fibres in polyetheretherketone (PEEK)

This materials represent a broad spectrum of fibre reinforced plastics, including both thermo-curing and thermo-plastic matrix materials, and also glass as well as carbon fibres. In most cases the matrix material as well as the fibre material was tested for hydrogen uptake by gravimetric measurements (see Section 3, **Permeability and Solubility**). Mechanically only the finished composite materials were tested.

Appendix 1 gives further data describing the materials used for the experiments.

3 Permeability and Solubility

The application of materials in containers for storage of liquid gases requires the material to be largely impermeable to the stored gas and to the surrounding gas. This must be true at the ordinary service temperature as well as at any temperature the system may reach by various conditions which may appear. The interesting gases in the present case are liquid hydrogen and liquid natural gas, i.e. liquid methane.

The need for impermeability can be met by utilisation of a liner, a thin layer of impermeable material, which does not necessary have a structural function in the construction. That method is treated in a number of the references found in the literature search described in Section 1. A more simple and direct solution to the problem, however, would be the application of a impermeable, structural material.

The temperature of liquid hydrogen at 1 bar is close to 20 K and for liquid methane the temperature is approx. 104 K. Since it is difficult and expensive to do experimental observations at 20 K, it was decided to accept the temperature of boiling nitrogen at 1 bar (approx. 77 K) as an indicator for the permeability properties of materials at low temperatures. Positive results, understood as low permeabilities, found at 77 K was considered as evidence for positive results also at lower temperatures. This is due to the fact, that diffusivities of gases in solids decrease rapidly with decreasing temperature.

The selected materials in the present project were tested for gas uptake in a beam type ultra-microbalance, which could be pressurised to. Aluminium was used to counterbalance the beam, and that was necessary to apply the highest sensitivity range of the balance.

The low testing temperature (77K) was provided by immersing both the reference and the sample hangdown-tube of the microbalance into a dewar containing liquid nitrogen. The dewar was fabricated specially for the purpose, and was made from glass fibre reinforced polyester. The boil off rate of the liquid nitrogen was approx. 0.5 *l*/h.

A sketch of the set-up is seen in Fig. 3.1 and a photograph of the balance and the dewar is shown in Fig. 3.2. Since all experiments were run at constant temperature, no buoyancy effects had to be taken into account.

As the weighing measurements were anticipated to be of rather long duration, the time stability of the balance equipment was tested over days prior to running the experiments themselves. The result of this stability test is shown in Fig. 3.3. Over a period of three days and nights (more than 60 hours), the weight reading varied within limits of ±10 micro-g. This result was considered sufficiently satisfactory to proceed with the measurements. It may be noted here, that all the figures in the present re

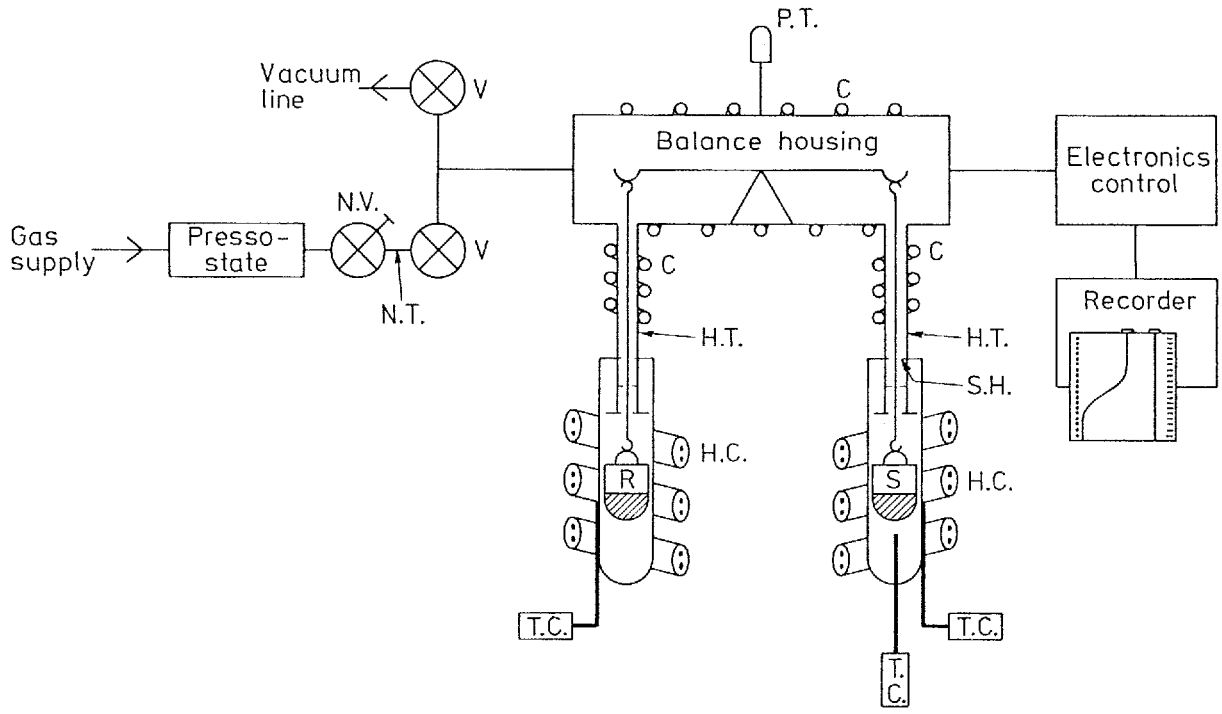


Fig. 3.1 Sketch of the balance set-up used for the permeability measurements in the present work.

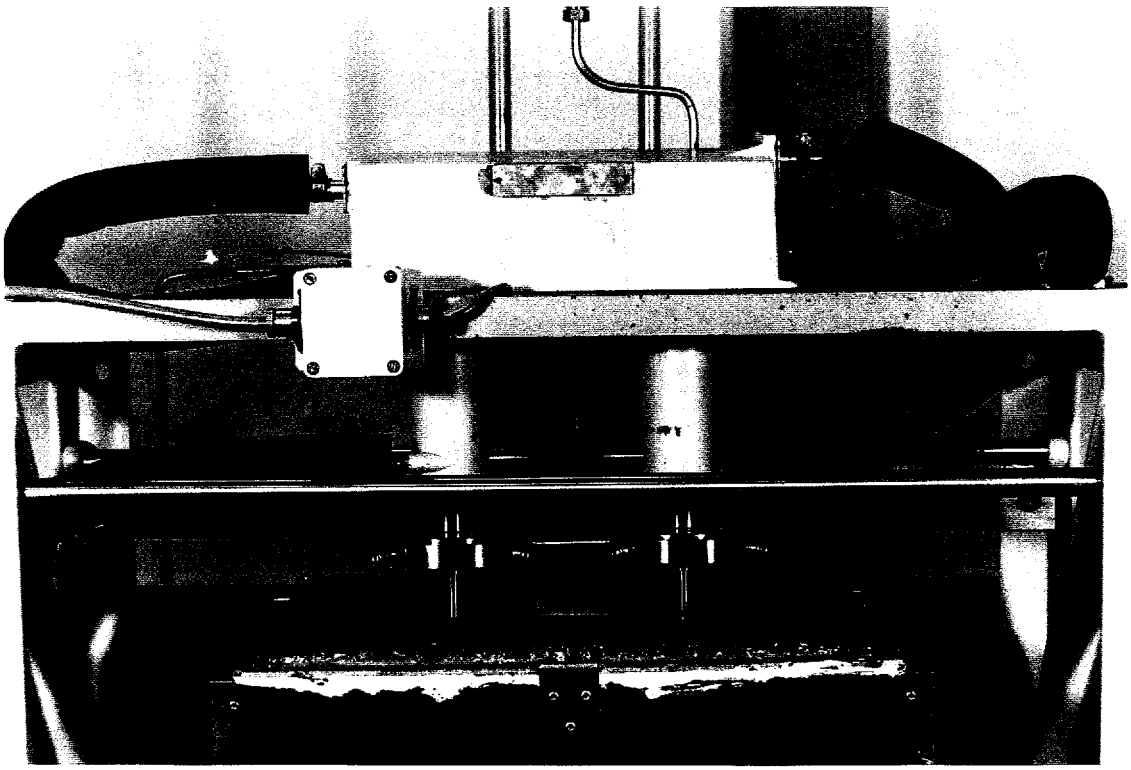


Fig. 3.2. Photo of the micro-balance and the dewar used for nitrogen

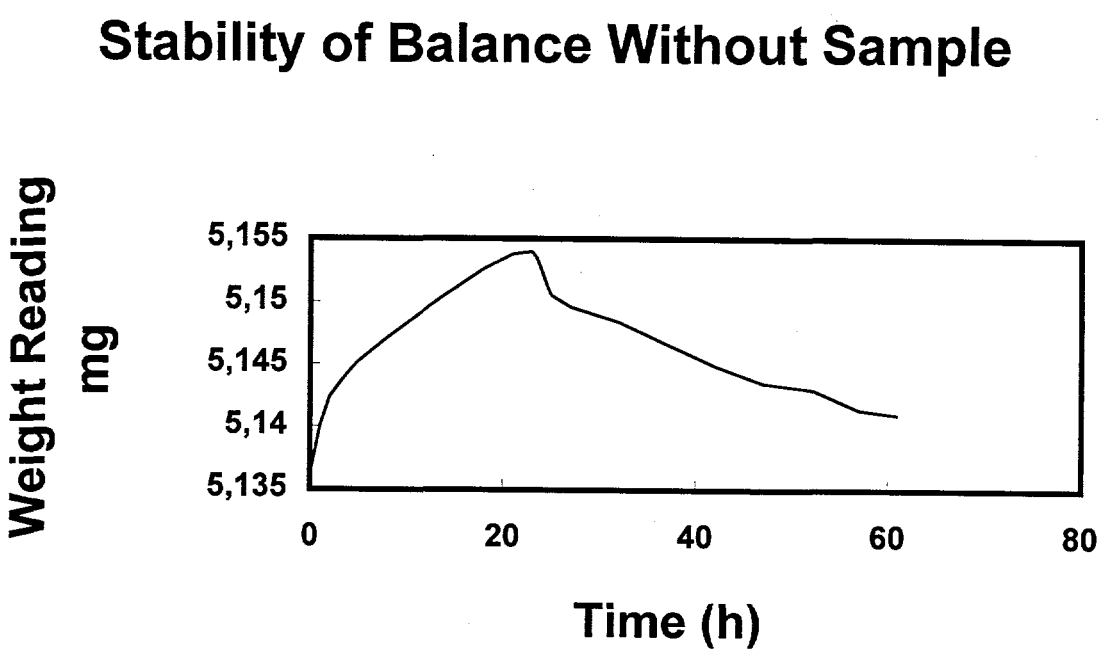


Fig 3.1. Weight recording showing the stability over 60 hours.

port showing results from balance experiments have been obtained by manually transferring paper-recorded data to electronic spread sheet. The manual transfer has limited the number of data points which implies minor apparent indifferentiabilities in the curves. These were not found in the original paper recordings.

Table 3.1 (next page) gives an overview of the samples used for the weight measurements and some key experimental data.

The weighing experiments were started by evacuating the equipment to better than 10^{-3} mbar before letting in gas (the balance was evacuated by a turbomolecular pump, which has an ultimate residual gas pressure better than 10^{-7} mbar, but the pressure gauge was not able to measure pressures below 10^{-3} mbar). The gas pressure used in all experiments was 2 bar. Very often an initial weight loss from the polymer samples was observed after letting in pure (dry) gas. Therefore all experiments were started in He and the reaction gas was not let in until constant weight in He was reached. This initial weight loss was ascribed to the release of solvents and moisture in accordance with the materials specifications as given in Appendix 1. The outgassing procedure was done at room temperature to obtain the fastest possible release of volatile species.

After obtaining stable weight readings, the temperature was set to the desired experiment temperature (room temp. or 77 K). The He was then exchanged (by evacuation) with reaction gas (hydrogen or methane) and

Table 3.1 Overview of Samples Measured by Gravimetry

Material (see Appendix)	Sample ID	Figure no.	Temperature	Gas	Sample Weight	Spec. Surf. Area	Max Uptake Rate
			K		g	cm^2/g	$\mu g/g \cdot cm^2$
Alpolit UPS 294v	UPS	4	300	He/CH_4	0.4162		
Alpolit UPS 294v/glass	UPSGLAS	5	300	He/H_2	0.4168	11.0	90
Alpolit UPS 294v	PS294v	6	300	He/H_2	0.4169	6.2	170
APC 2	APC 2	7	300	He/H_2	0.4211	15.7	60
M40 B	M40 BCar		300	He/H_2	0.3713		
APC 2	APC2_2	8	300	He/H_2	0.3933	75.5	10
Epoxy	Epoxy3	9	300	He/CH_4	0.4165	6.7	140
Epoxy/Carbon	EpoxyCar	10	300	He	0.3927	8.9	110
Epoxy	Epoxy1	11	300	He/H_2	0.2843	9.1	110
PEEK	PEEKCH4	12	300	He/CH_4	0.3975	379.4	3
PEEK	PEEK77H2	13	77	He/H_2	0.4150	361.5	3
PEEK	PEEKHeH2	14	300	He/H_2	0.4227	354.9	3
PEEK	PEEKH2	15	300	He/H_2	0.5230	307.5	3
Nil	Nil	3	300	Air			

the weight changes were recorded as a function of time while maintaining constant temperature.

Figures 3.4 through 3.15 show the weight recordings for the tested materials. Temperatures and gases are indicated in the figure legends. The sample ID M40BCar was a pure carbon fibre. During the weighing experiment with this sample the weight was completely constant in first helium and then hydrogen. Therefore the results of this experiment is not shown in a figure.

All samples were run at room temperature because the uptake of gas was considered to be most fast at that temperature due to the temperature dependence of the diffusivity. This assumption was confirmed by low temperature measurements on sample PEEK77H2 (see Fig. 3.13) as can be seen by comparison of the data in Fig. 3.13 with the data in Fig. Fig. 3.14 and Fig. 3.15.

In general we were not able to detect any uptake of hydrogen or methane by the described procedure. Because of the mentioned release of volatile components, the sample mass was actually not strictly constant in any case when the reaction gas was let in. The weight was actually decreasing weakly at that point. In principle therefore the weight curves may reflect the net result of two opposite phenomena: 1) release of volatile components and 2) uptake of reaction gas. However, inspection of the slopes of the weight curves before and after the gas exchange shows, that a possible take-up was at least smaller than the detection limit of the measurements.

The problem of gas diffusion in the x-direction into a solid is described by the diffusion equations. For gas in contact with a metal surface the boundary conditions are

1) At time $t = 0$ the concentration of gas C_S at the surface ($x=0$) is the saturation concentration and the gas concentration equals 0 for $x \neq 0$ in the solid.

2) $C \rightarrow C_S$ for any x as $t \rightarrow \infty$.

These boundary conditions correspond to a sudden gas exposure at $t = 0$ and complete saturation of the solid at infinite time. The solution to the diffusion equation for these boundary conditions is:

$$C(x,t) = C_S \left[1 - \mathrm{erf}\left\{\frac{x}{2\sqrt{Dt}}\right\}\right]$$

where C_S is the saturation concentration, D is the diffusion coefficient, x is the distance from surface and t the time since start of exposure.

The uptake speed thus depends on both the gas/solid contact area, the saturation concentration and on the diffusivity. In the present experiments we were not able to measure the saturation concentration, since we were not able to detect any uptake at all. The detection limit in the measurements was about 1 mg/g per hour. This finding can be converted to uptake per sample surface area unit (which is the parameter of interest to practical applications) by use of the numbers for specific surface area given in Table 3.1. In those terms the uptake rate is less than the numbers shown in Table 3.1.

The conclusion from the described experiments is, that with the exception of PEEK all examined matrix materials showed no measurable uptake at room temperature. This means that the uptake rates were less than given by the numbers in Table 3.1, which in turn means that diffusion of hydrogen and methane through these materials can be disregarded (diffusion losses through container walls).

PEEK did show an uptake at room temperature of methane as well as hydrogen. The largest uptake rate measured was approx. 2 mg/cm^2×h for methane. For a spherical container of diameter 1 m (volume about 500 *l*) the surface area is about 3 m^2, which would give a maximal diffusion loss through the walls of 20 mg/h assuming an uptake rate of 2 mg/cm^2×h. This number may not be ignorable under all circumstances. However, at the temperature of liquid nitrogen, the uptake of hydrogen in PEEK went to a complete stop. Therefore diffusion losses through container walls can also be disregarded for this material at the application temperature.

The carbon fibres used in the samples were tested for reaction (possible uptake) with hydrogen. No reaction was detectable at all and a completely steady line was obtained for the weight over a period of 7 h.

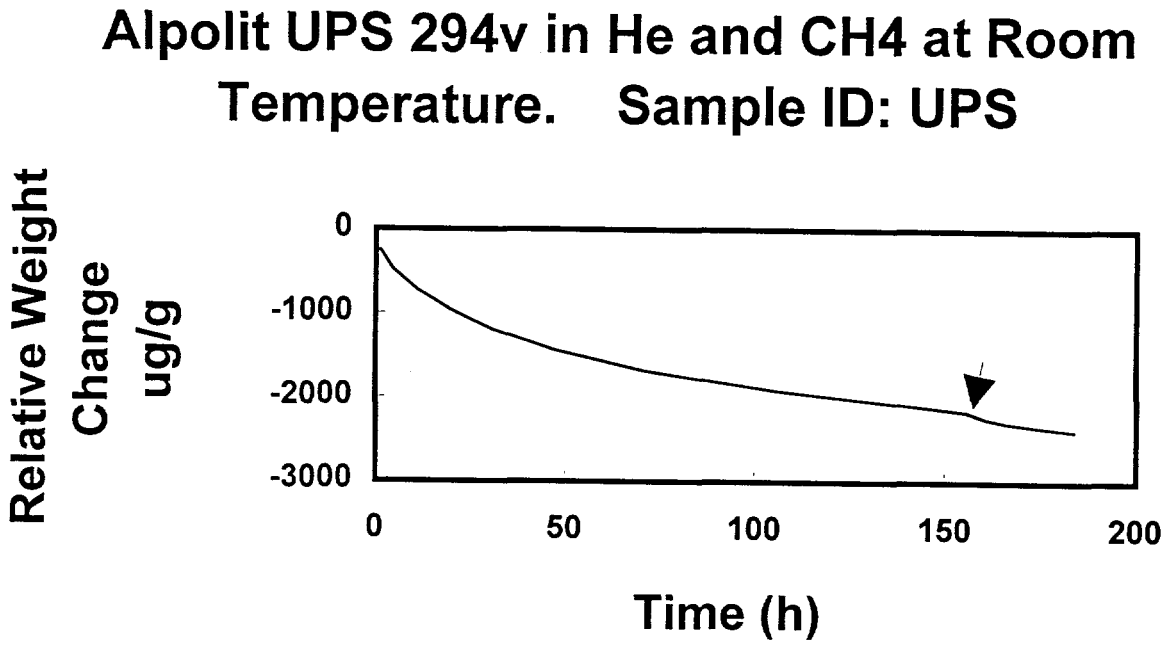

Alpolit UPS 294v in He and CH4 at Room Temperature. Sample ID: UPS
Relative Weight Change ug/g
0
-1000
-2000
-3000
0
50
100
150
200
Time (h)

Fig. 3.4

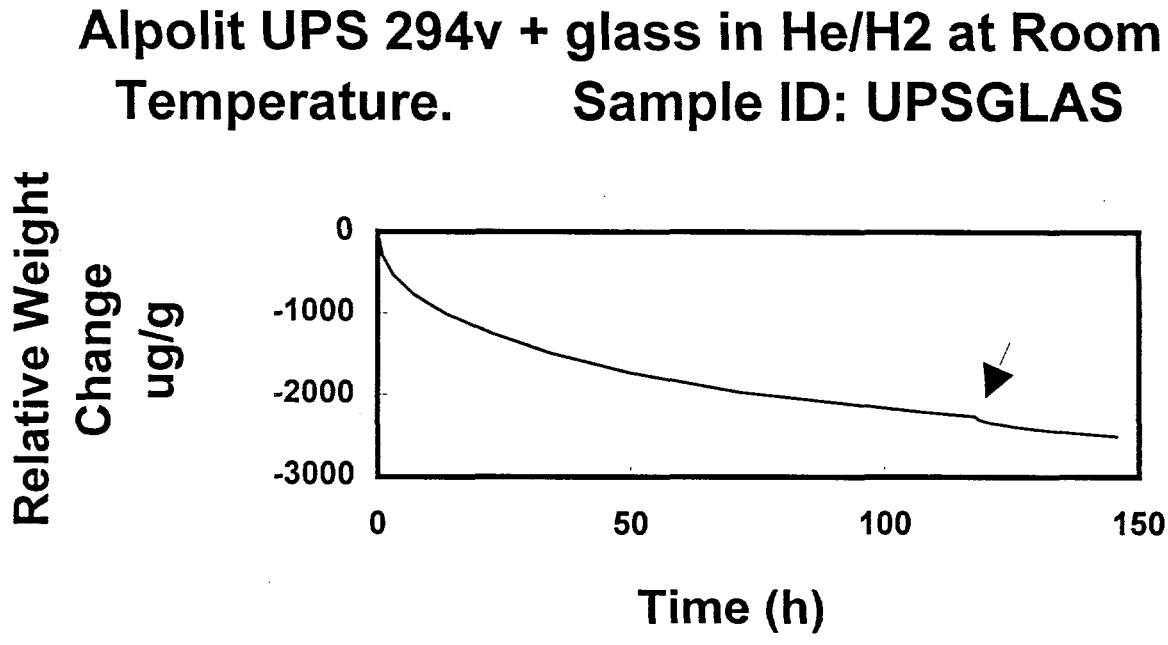

Alpolit UPS 294v + glass in He/H2 at Room Temperature. Sample ID: UPSGLAS
Relative Weight Change ug/g
0
-1000
-2000
-3000
0
50
100
150
Time (h)

Fig. 3.5

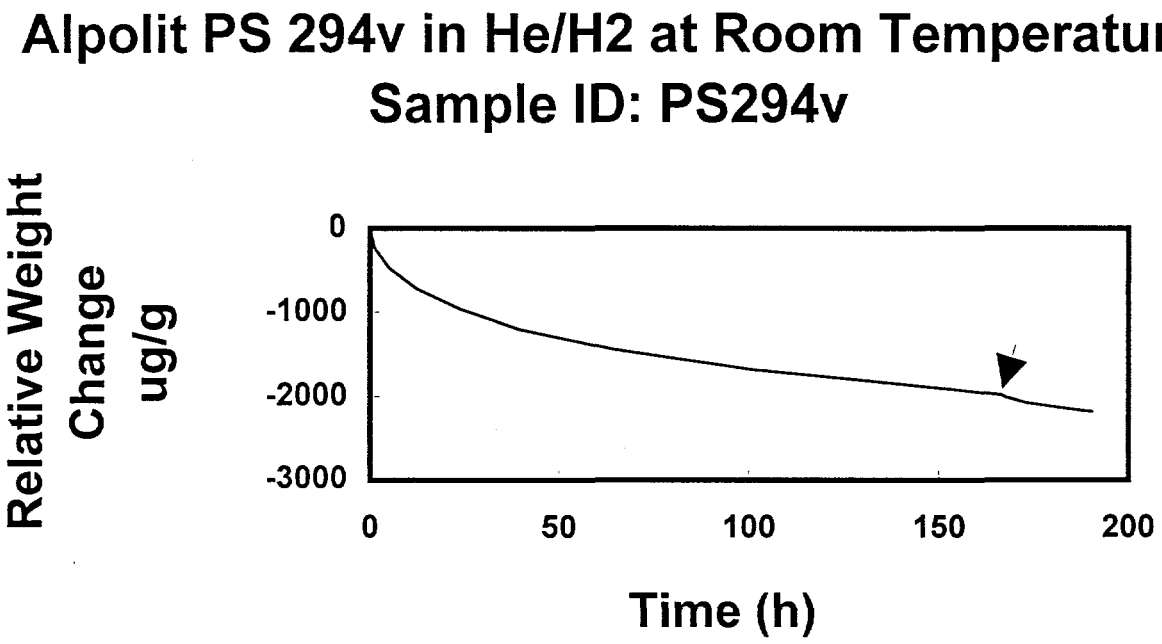

Alpolit PS 294v in He/H2 at Room Temperature
Sample ID: PS294v
Relative Weight Change ug/g
0
-1000
-2000
-3000
0
50
100
150
200
Time (h)

Fig. 3.6

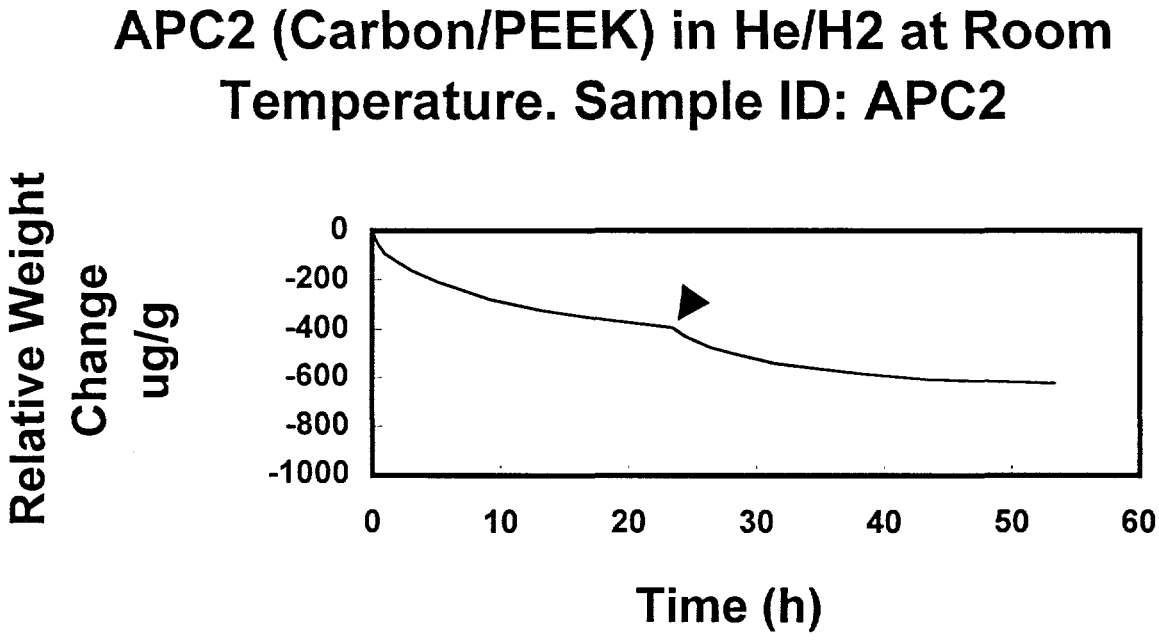

APC2 (Carbon/PEEK) in He/H2 at Room Temperature. Sample ID: APC2
Relative Weight Change ug/g
0
-200
-400
-600
-800
-1000
0
10
20
30
40
50
60
Time (h)

Fig.3.7

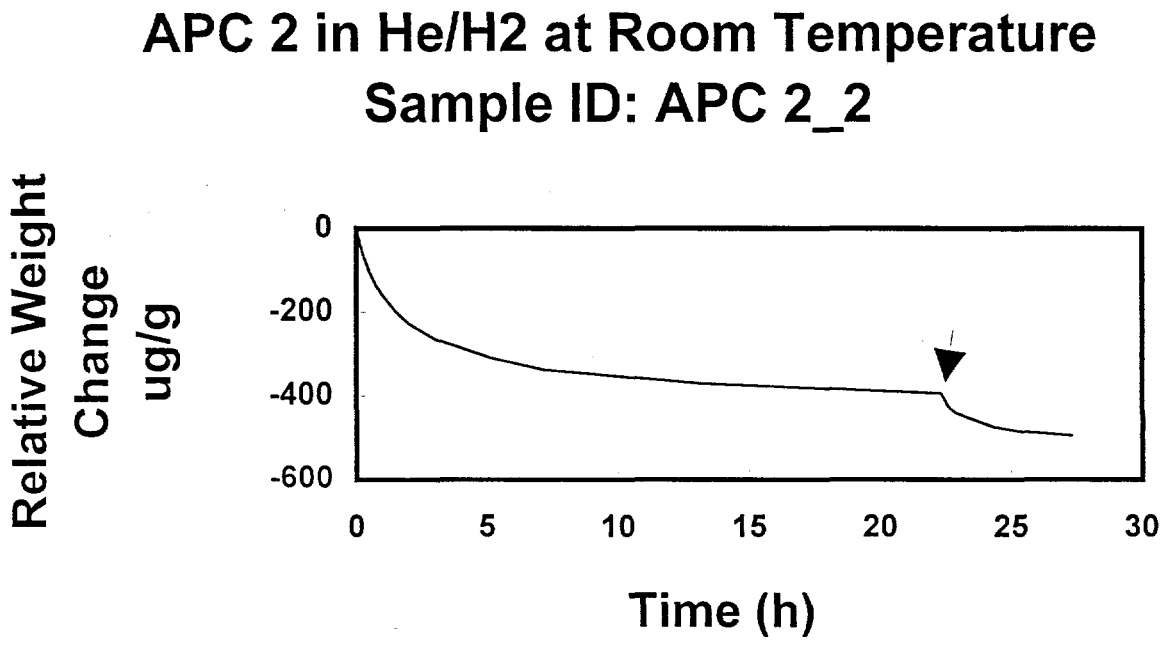
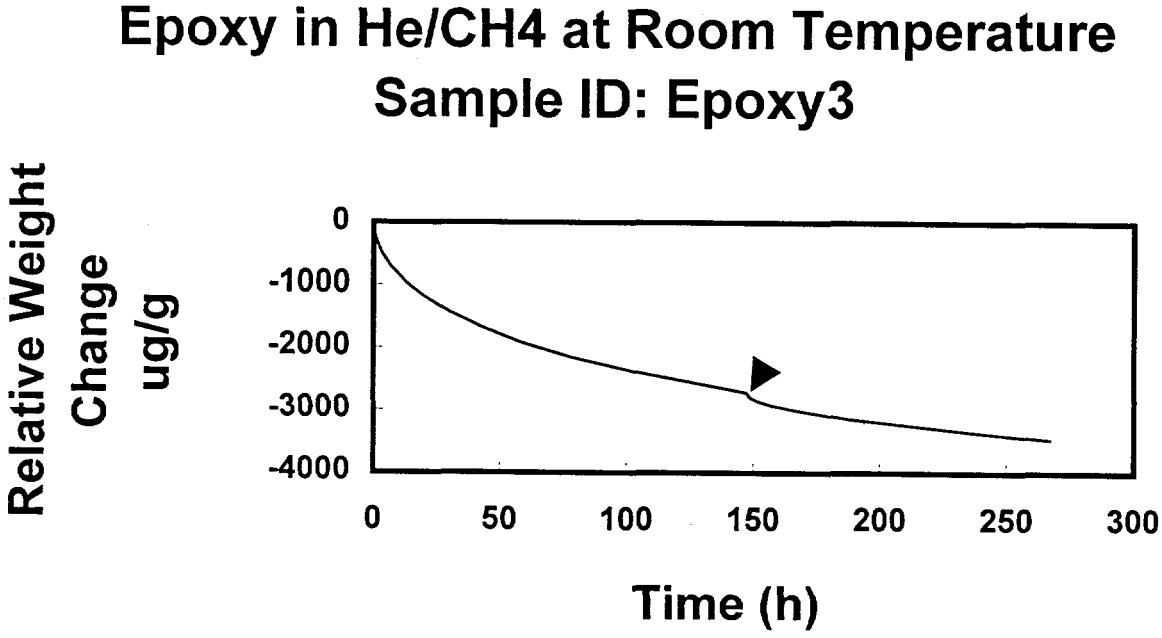

APC 2 in He/H2 at Room Temperature
Sample ID: APC 2_2
Relative Weight Change ug/g
0
-200
-400
-600
0
5
10
15
20
25
30
Time (h)

Fig. 3.8


Epoxy in He/CH4 at Room Temperature
Sample ID: Epoxy3
Relative Weight Change ug/g
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-1000
-2000
-3000
-4000
0
50
100
150
200
250
300
Time (h)

Fig. 3.9

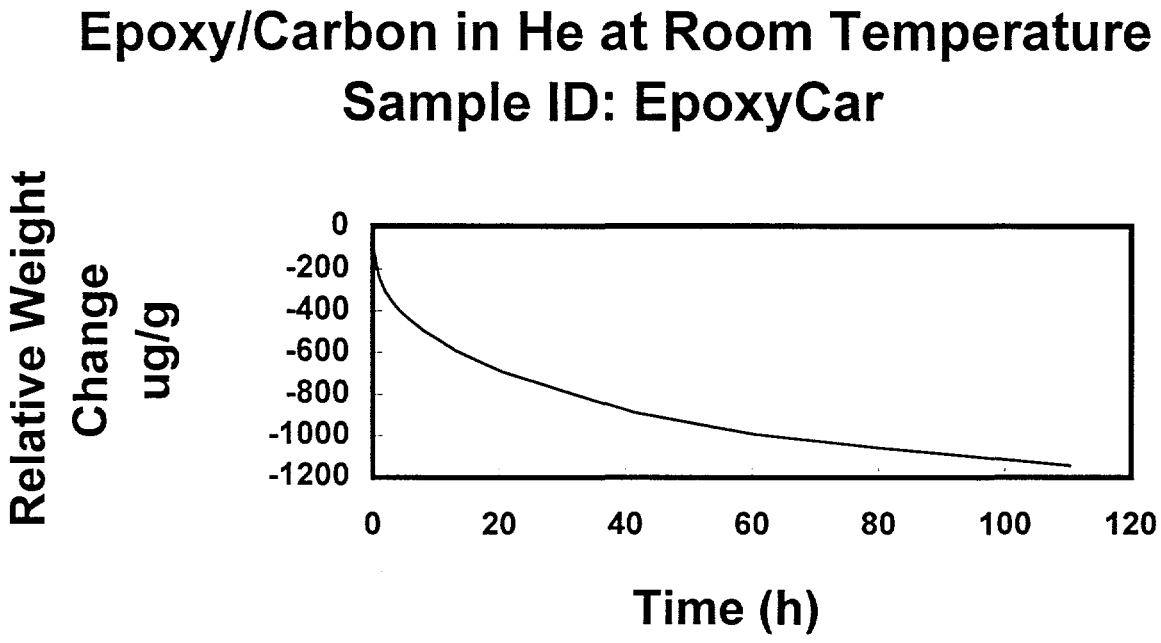

Fig. 3.10

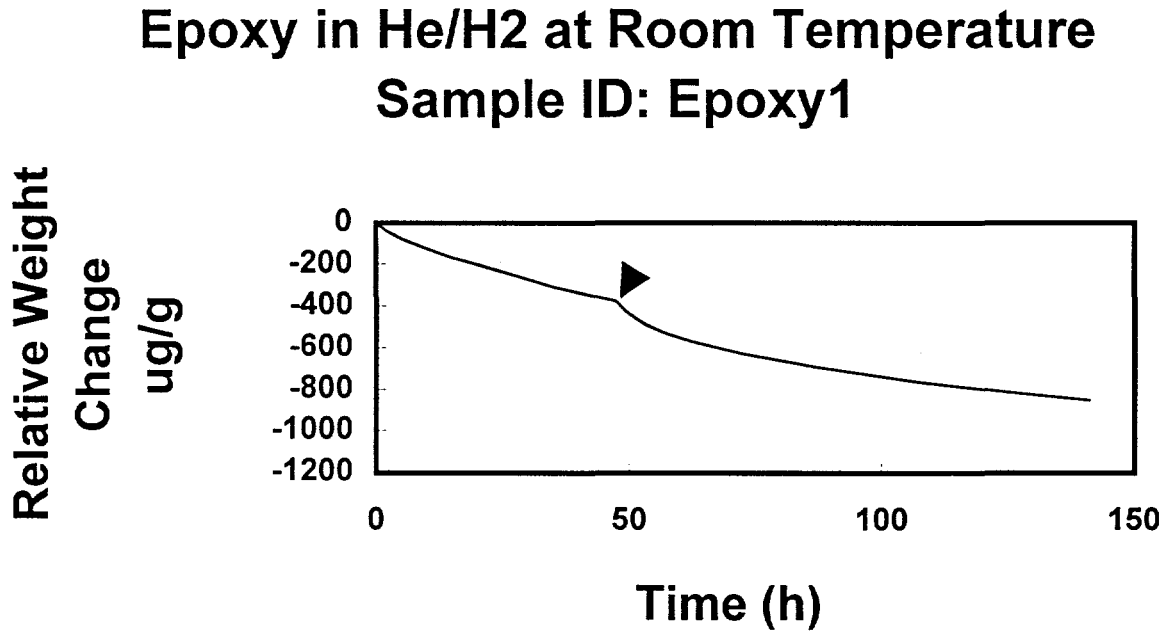

Fig. 3.11

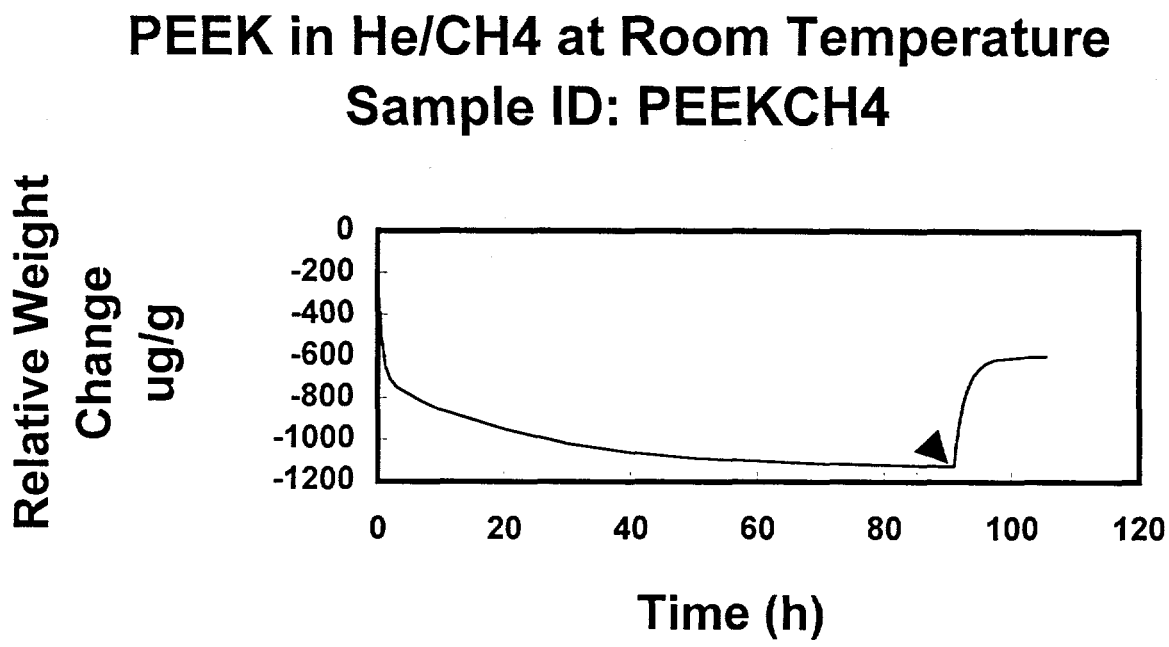

Fig. 3.12

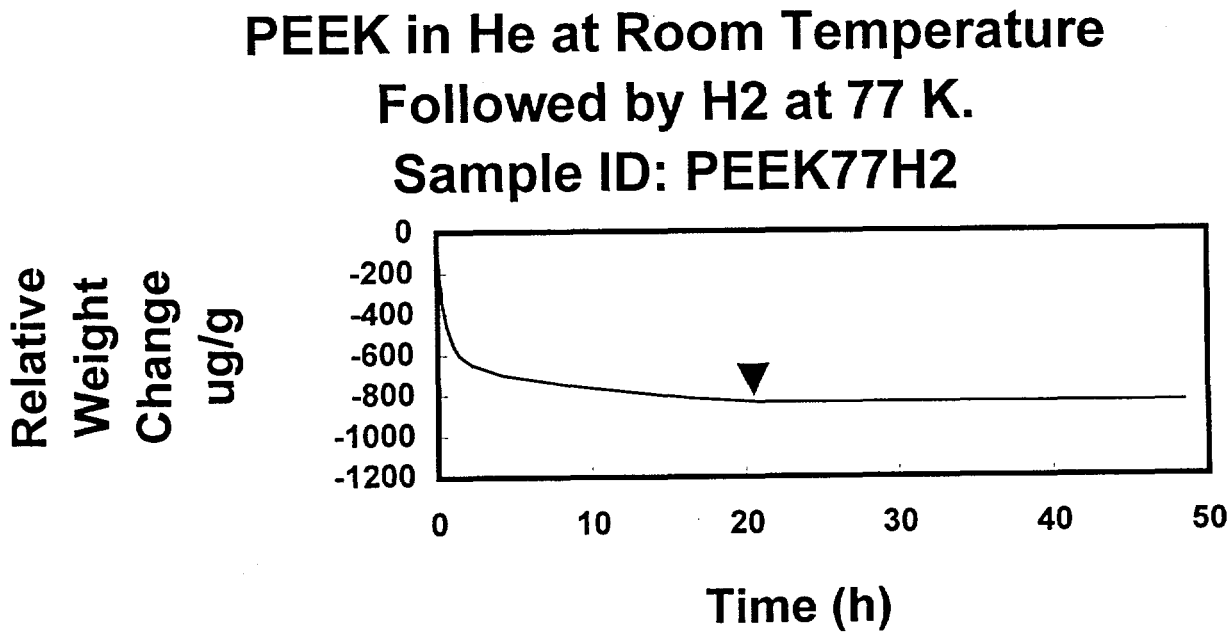

Fig. 3.13

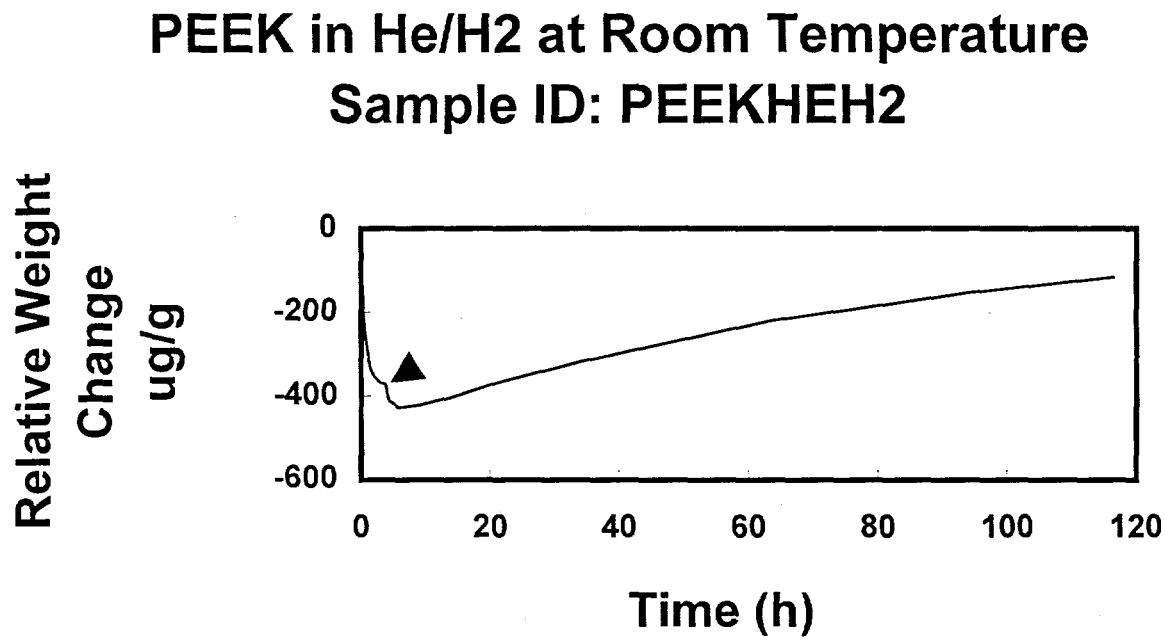

Fig. 3.14

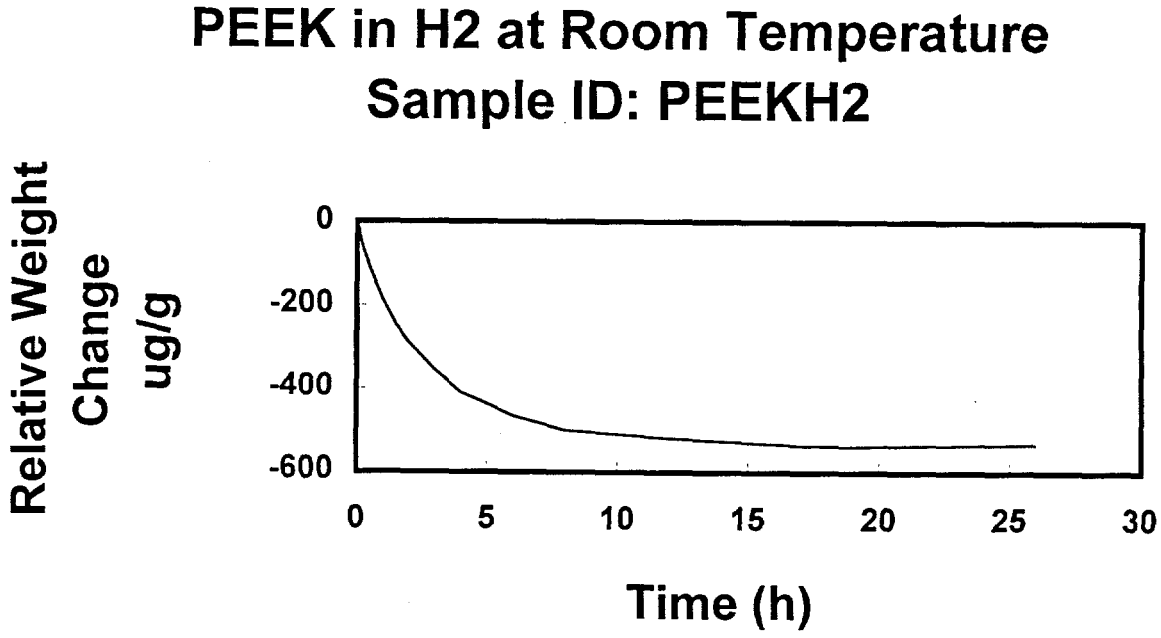

Fig. 3.15

4. Mechanical Testing

The purpose of testing the materials mechanically was to identify the conditions for crack formation in the matrix material at low temperatures, where the organoplastic matrix materials become very brittle compared with the properties at room temperature. If a crack forms in a liquid gas container, there is a considerable risk, that gas molecules will diffuse through the walls and hazardous gas formations may build up.

4.1. Sample preparation

Samples were prepared from the same base materials as characterised by the gravimetric measurements. The following combinations and fibre angles were used:

Table 4.1. Overview of Samples Prepared for Mechanical Testing

Sample No.	Material	Fibre Orientation
1	Glass/Polyester	0°/90°
3	Glass/PET	0°/90°
4	Glass/Epoxy	0°/90°
5	Carbon/Epoxy	0°/90°
6	Carbon/Epoxy	0°/90°
7	Carbon/PEEK	0°/90°
8	Carbon/PEEK	0°/90°

The sandwiches were composed of 4 - 8 layers, arranged symmetrically relative to the sample midplane. Initially the laminates were prepared in the form of plates, and then the test samples were cut from the plates following the 0° fibre direction. The shape and dimensions of the test samples are shown in Fig. 4.1. The 0° fibre orientation was chosen be

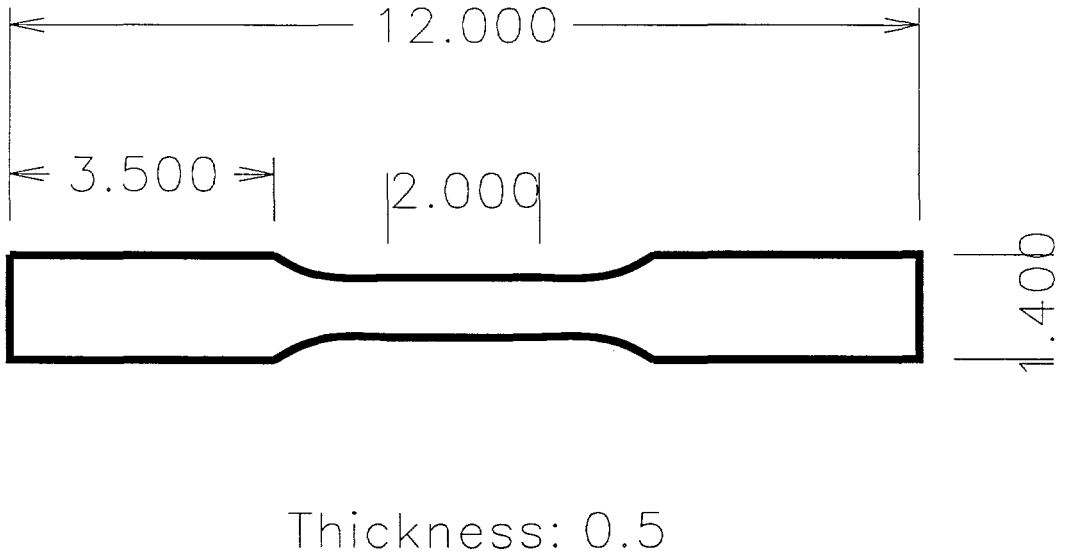

Fig. 4.1. Shape and dimensions of test samples for mechanical testing.

cause this type of laminate is very sensitive to matrix crack in the 0° fibre direction, when loaded in the 0° direction, and therefore a laminate well suited for evaluation of the crack sensitivity of the different materials combinations studied. Laminates used in pressure vessels will normally be less sensitive.

4.2. Mechanical Testing

The selected materials were characterised by tensile testing at the temperature of liquid nitrogen, -196 °C or 77 K. The testings were done under simultaneous recording of strain, load and acoustic emission from the sample.

The testings were done by immersing the samples in liquid nitrogen at atmospheric pressure. During the experiments the nitrogen was constantly boiling off the dewar and this process was suspected to be associated with acoustic emission itself. Therefore an initial experiment was done to test the viability of the method for registration of acoustic emission from the sample. The experiment showed, that the acoustic emission from the formation of bubbles did not interfere with the emission from the samples. No signal was detected from the boil-off of liquid nitrogen from the dewar.

7 samples were subsequently measured and the tensile load as well as the strain and the accumulated acoustic emission were recorded. The results (converted to stress) are shown in Figs. 4.2 - 4.8 for strains in the range from zero up to about 1 %.

One sample started to emit acoustic signals almost immediately after starting the experiment at very low strain. The results for this particular sample (Sample no.1) is shown in Fig. 4.2. We did not measure the crack dimensions, but on the background of the steep curve for accumulated acoustic emission the cracks are assumed to be serious.

The remaining samples showed only weak acoustic emission up to strains of about 0.3 % which corresponded to stresses in the range 100 - 150 MPa for the majority of the samples. One sample, however, (Sample no. 3) did not show significant emission even at strains up to 0.7 % or more. For that sample the corresponding stress was about 170 MPa and even at this value no sign of failure can be seen from the curves.

If a spherical geometry is assumed for a container fabricated from materials like the tested and the container is loaded by an internal pressure, then for a container of internal diameter 1 m and a wall thickness of 5 mm, a stress of 150 MPa corresponds to a pressure of 1.5 MPa or 15 Bar. This means that the pressure in such a container can raise to 15 bar before cracking starts. 15 bar is judged to be much higher than acceptable for

several other reasons, and consequently the measured strength of the materials seems to be more than sufficient.

The results of the mechanical tests show, that 6 out of the 7 tested materials combinations would be suitable for the construction of a low temperature liquid gas container as regarding the risk for crack formation and subsequent leakage. One material, the glass/PET - sample no. 3, however, seems to be somewhat better than the others.

Fig. 4.2 (opposite page high)

Fig. 4.3 (opposite page low)

Tensile tests and AE with gain and threshold

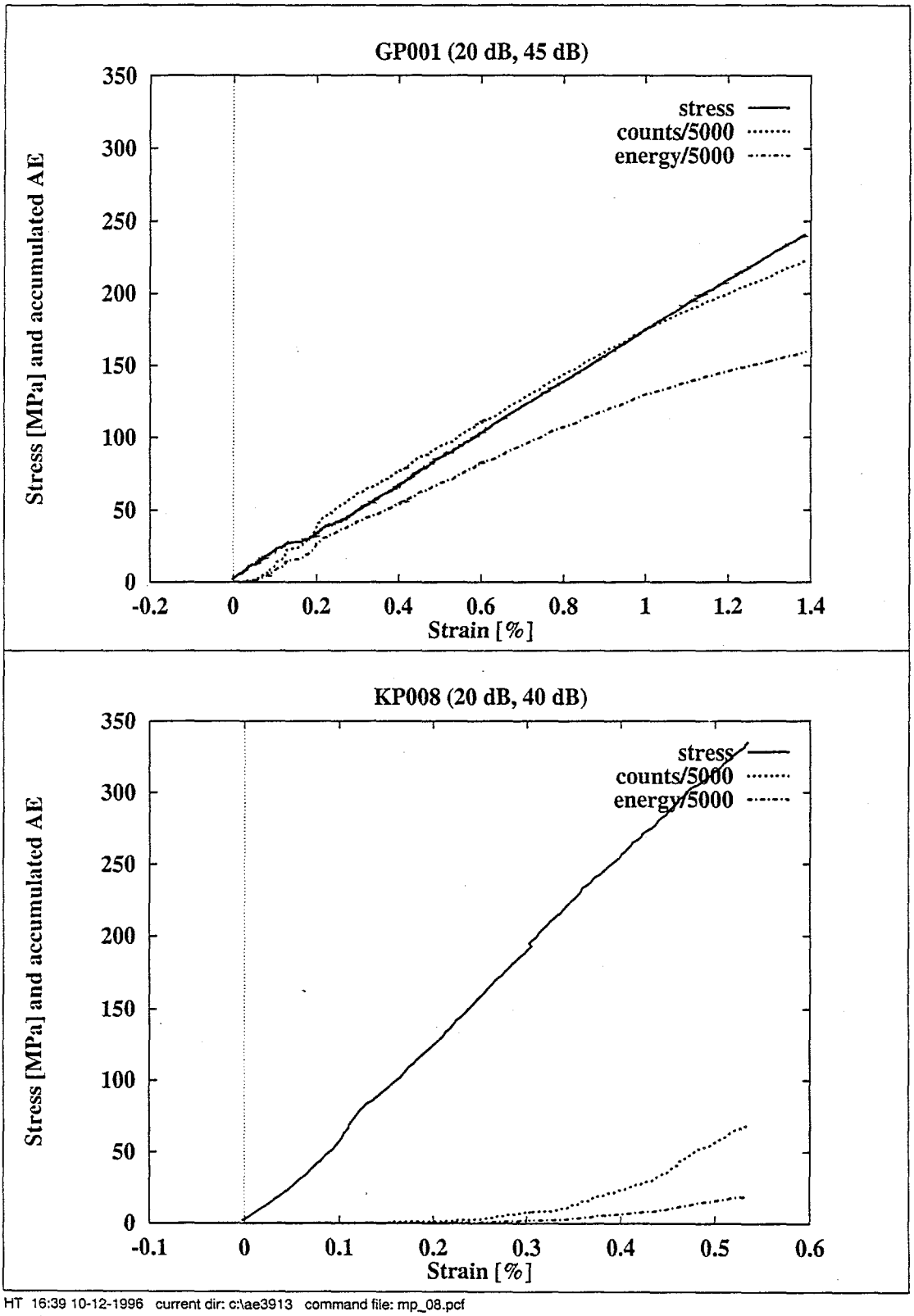

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Fig. 4.4 (opposite page high)

Fig. 4.5 (opposite page low)

Tensile tests and AE with gain and threshold

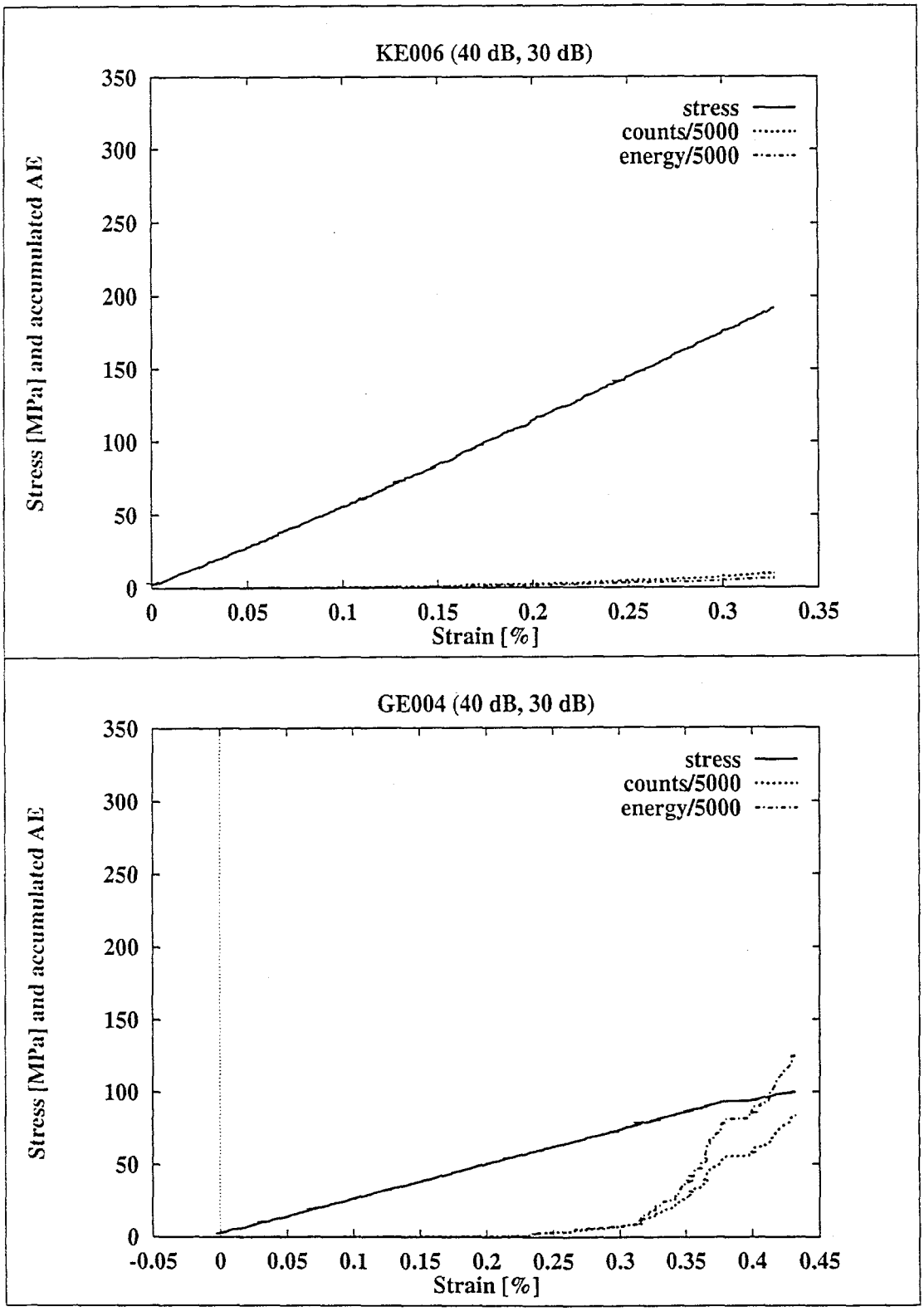

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Fig. 4.6 (opposite page high)

Fig. 4.7 (opposite page low)

Tensile tests and AE with gain and threshold

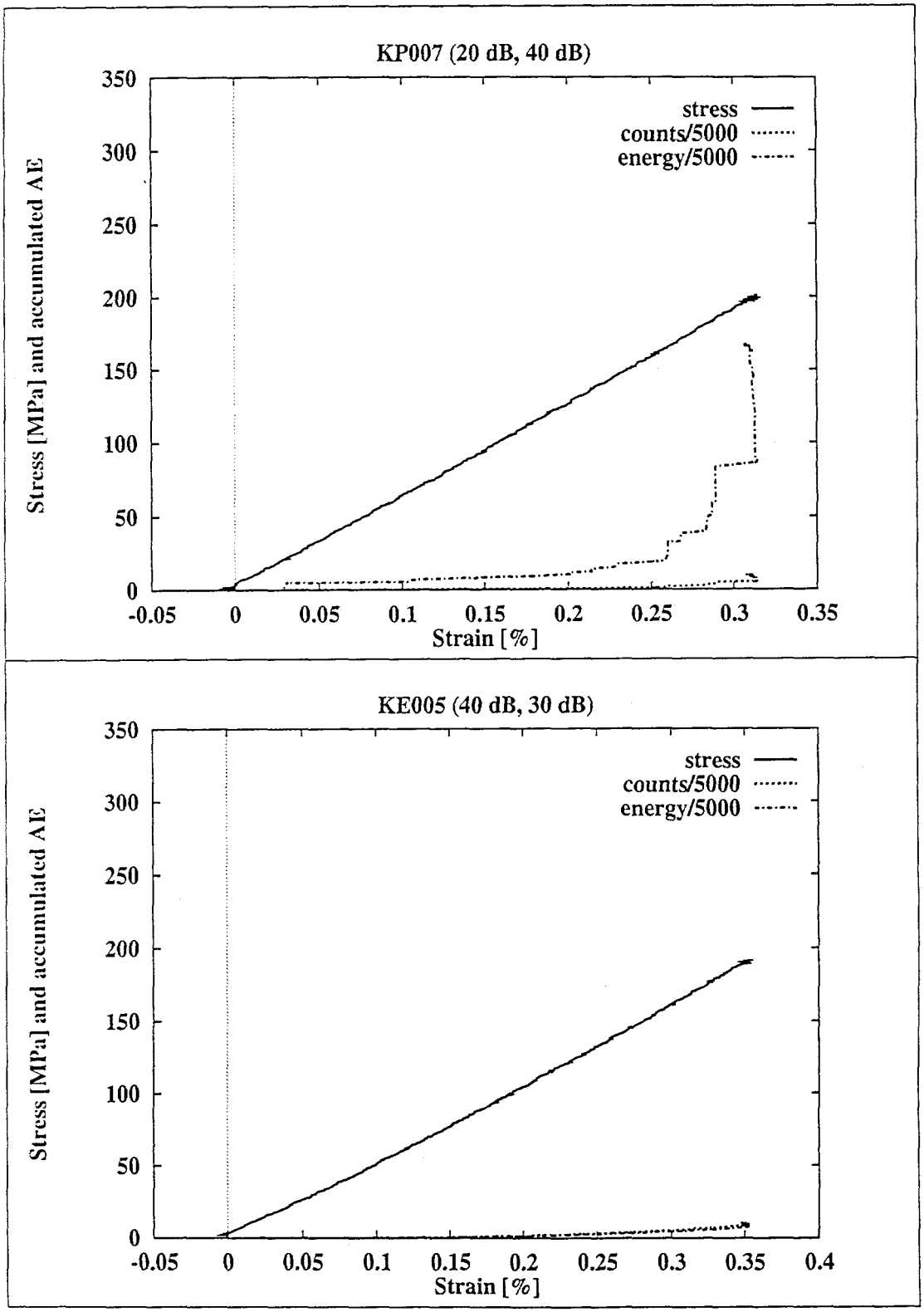
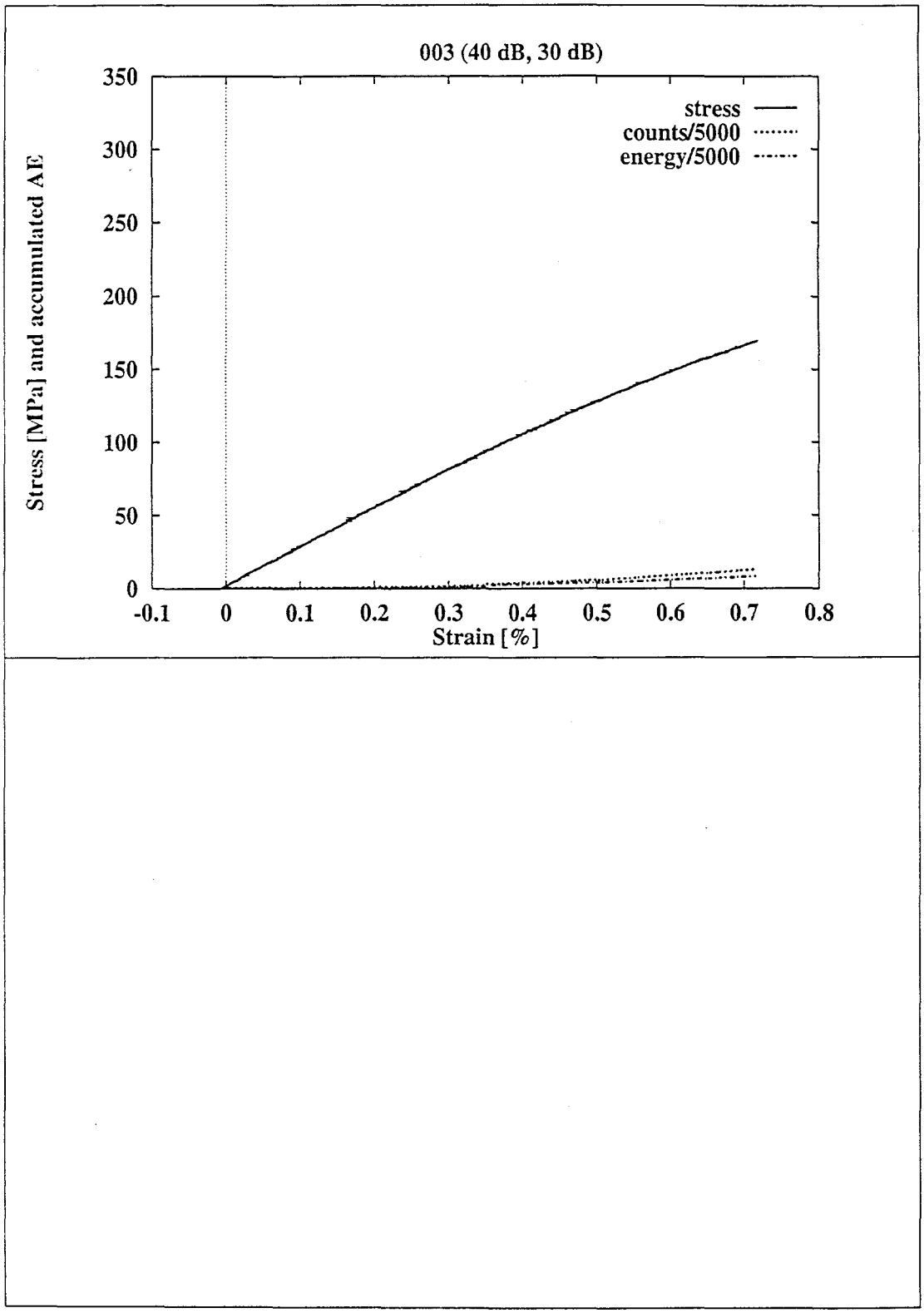


Fig 4.8 (opposite page)

Tensile tests and AE with gain and threshold



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RISØ

5. Considerations on Safety and Economy.

5.1 Safety

Traditionally combustible gases are considered to be extremely hazardeous, and in particular so hydrogen. On the other hand hydrogen and natural gas both in the gaseous and in the liquid state has become a commodity with increasing large-scale distribution and use in the modern society.

More objectively the hazardous properties of liquid hydrogen has been investigated experimentally by a number of laboratories and the work done at the US Department of Energy´s test site in Nevada during the eighties shall be mentioned here[1].

The precautions necessary when handling cryogenic fuels are to a last extent identical to those necessary when handling gaseous fuels. The combustion of fuels requires the simultaneous presence of three things: The fuel, an oxidiser and an ignition source. Most hazard prevention measures rely on the absence of at least one. However, a number of aspects are specific to the liquid state.

Thermal gradients may cause stresses in construction materials. Under well-defined conditions, such stresses can be standard calculation techniques. Transient thermal gradients, for instance under cooling processes, may be more unpredictable and therefore also more hazardous. The technical area of thermal gradients in materials should certainly be treated in future projects on development of cryogenic containers in plastic composites.

Materials compatibility. Plastic composites used for cryogenic containers must be able to serve at the low temperatures for prolonged times and no chemical reaction should take place between the cryogenic liquid and the container material. This issue has been addressed preliminary by the work in the present project.

Pressure buildup. Cryogenic fluids constantly evaporate to an extent determined by the isolation efficiency of the container holding them (liquid hydrogen even evaporates under total heat isolation due to the so called ortho-para reaction taking place in naturally occurring hydrogen). If the container can be closed completely there is a risk for pressure buildup. During normal service the evaporated gas should be vented.

---

[1] Safety Aspects of Large-Scale Combustion of Hydrogen", F.J.Edeskuty, J.J.Haugh and R.T.Thompson, Hydrogen Energy Progress VI, Proceedings of the 6th World Hydrogen Energy Conference, Vienna, Austria, 1986.

Disposal of gas is necessary due to the above mentioned evaporation of gas. For small evaporation rates, e.g. rates below 1-2 g/s, the boill-off can be vented to atmosphere without flaring. For higher rates, e.g. more than 100-200 g/s flaring would usually be recommendable.

Condensation of impurities is hazardous at low temperatures. The temperature of liquid hydrogen is low enough to condensate and solidify atmospheric air. The vapor pressure of solid air is extremely low, and therefore nothing will warn about the presence of solid air (solid oxygen). Therefore contact between air and liquid hydrogen or other combustible, cryogenic liquids should be avoided.

5.2 Economy

In Denmark the commercial distribution of hydrogen and natural gas is done in the gaseous state in traditional metal high pressure vessels. In many other countries (e.g. France, Germany, USA), however, distribution of hydrogen in large quantities is done in the liquid state. The containers used for that purpose are usually made of stainless steel (often 304). A shift to plastic composite materials would imply a weight saving, the size of which can not be specified on the basis of the presently available data.

There is a well-established plastic composite industry in Denmark which has produced advanced materials for decades. This industry is capable of producing also materials for storage of cryogenic liquids.

An important point in society economy is, that commercial containers for liquid gases would provide the background for application of hydrogen and natural gas in the transportation sector. The impact of such a shift to a hydrogen technology scenario would not lead to a better economy in general, but rather to better environmental conditions due to improved (lower) emission of toxic compounds from engines. A shift to LNG would probably imply both environmental and economic improvements, at least in countries possessing their own natural gas resources (like Denmark).

A major problem in shifting fuel in the transportation sector is the required change of infra-structure. Whereas the present infra-structure is dedicated to fossil liquid fuels (gas and Diesel oil), a considerable investment in new infra-structure and in the learning of new practices would be necessary for a switch of fuel (see e.g. Morthorst et al., Risø-R-675(DA)).

6 Conclusions and Recommendations

The literature search has shown, that only relatively few laboratories has world-wide until now worked with plastic composite materials as a first wall in containers for storage of low temperature liquid gases like hydrogen or natural gas. The work done until now has dominantly been concentrated in the space and aircraft industry. On the other hand the literature search has also demonstrated, that there is an increasing interest in the subject, perhaps particularly in the USA, where a 3 million US$ research and development programme on new technologies for storage of Liquid Natural Gas has been launched by the Department of Energy. Also in Europe an increasing interest is found, illustrated by for example the German MAN-Technologie.

In the experimental part of the present project a limited series of experiments have been carried out, aiming at describing the properties of a number of selected plastic composite materials in relation to their utilisation as construction materials for liquid gas containers. The experiments have been concerned with the measurement of gas diffusion through the composite materials and with the mechanical properties at low temperatures.

Gas diffusion into the materials was measured by gravimetry in an ultramicrobalance. No uptake of gas was found at 77 K for any of the measured materials or materials combinations over periods of 25 - 50 hours. For the majority of materials no uptake could be detected even at room temperature. In one case, PEEK,an uptake was mesured at room temperature, but the rate was so low that it could be concluded not to represent a hazard in practice.

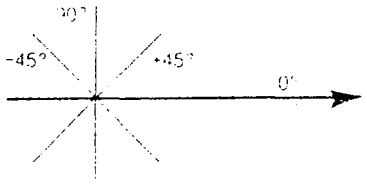
The mechanical properties of 7 composite samples were measured by tensile testing and simultaneous recording of the accumulated acoustic emission caused by crack formation. In 1 measurement out of 7 the acoustic emission indicated crack formation at relatively low stresses (ie. below 150 MPa. The rest of the samples only showed negligible acoustic emission up to 150 MPa, which is considered to be sufficient for application of the material in a liquid gas container.

The work done in the project indicates that plastic composites are suitable for application in low temperature gas containers. More exhaustive measurements of hazard-related physical and chemical materials properties are needed though, before a pilot container can actually be designed. In particular the reaction of the materials to long-term gas exposure needs to be characterised, and also more dedicated diffusion experiments should be carried out, recommendably done in a diffusion cell, where the material to be tested can be suspended as a diafragm separating a pressure difference.

Experiments should also be designed to test the mechanical properties of the composite materials at the actual temperature of liquid hydrogen and natural gas. The boiling point of hydrogen at atmospheric pressure is about 20 K, which is 57 K below the test temperature applied in this project.

Finally it is recommended to study the reaction of the materials to continued temperature cycling between ambient temperature and the low service temperature. This study should incorporate the aspects of fatigue as well as temperature chock resistance.

Appendix 1



APC-2
PEEK/CARBON FIBRE COMPOSITE

FIBERITE

DATA SHEET 3a:

Property data of aromatic polymer composite, APC-2/Hercules Magnamite® AS4 carbon fibre

APC-2: PEEK*/carbon fibre composite is an advanced structural composite of a proprietary high strength, unidirectional continuous carbon fibre in a PEEK matrix.

PHYSICAL PROPERTIES

Density	1.6 g/cm^3 (0.058 lb/in^3)
Carbon fibre volume fraction	61%
Carbon fibre weight fraction	68%
Carbon fibre areal weight	145 g/m^3

COEFFICIENT OF THERMAL EXPANSION

Fibre Orientation	Temperature	
0°	23°C-143°C (73°F-289°F)	0.5×10^{-6}/°C (0.28×10^{-6}/°F)
	143°C-343°C (289°F-649°F)	1.0×10^{-6}/°C (0.56×10^{-6}/°F)
90°	23°C-143°C (73°F-289°F)	30×10^{-6}/°C (17×10^{-6}/°F)
	143°C-343°C) (289°F-649°F)	75×10^{-6}/°C (42×10^{-6}/°F)

MECHANICAL PROPERTIES

Property	Test Method	Temperature		
0°	ASTM D-3039	23°C(73°F)		
Tensile strength			2130 MPa	309 ksi
Tensile modulus			134 GPa	19.4 msi
Tensile strain to failure			1.45 %	
Compressive strength	IITRI Test	23°C(73°F)	1100 MPa	160 ksi
Flexural strength	ASTM D-790 Span-to-depth ratio 60:1	23°C(73°F)	1880 MPa	273 ksi
Flexural modulus			121 GPa	17.5 msi
90°	ASTM D-3039	23°C(73°F)		
Tensile strength			80 MPa	11.6 ksi
Tensile modulus			8.9 GPa	1.29 msi
Tensile strain to failure			1.0 %	
Flexural strength	ASTM D-790 Span-to-depth ratio 25:1	23°C(73°F)	137 MPa	19.9 ksi
Flexural modulus			8.9 GPa	1.29 msi
± 45°	ASTM D-3518			
Tensile strength		-73°C(-99°F)	267 MPa	38.7 ksi
		23°C(73°F)	300 MPa	43.5 ksi
		120°C(248°F)	221 MPa	32.0 ksi
Tensile modulus		-73°C(-99°F)	21.9 GPa	3.18 msi
		23°C(73°F)	19.2 GPa	2.78 msi
		120°C(248°F)	12.9 GPa	1.87 msi
Tensile strain to failure		-73°C(-99°F)	19.9%	
		23°C(73°F)	17.2%	
		120°C(248°F)	18.0%	

Stabar
HIGH TEMPERATURE FILMS

TECHNICAL DATA SHEET
STD 110

'Stabar' K200 PEEK Film

'Stabar' K200 non-crystallised polyetheretherketone (PEEK) film is thermoplastic film made by ICI from ICI's 'Victrex' PEEK aromatic polymer It is one of the family of 'Stabar' high performance films

'Stabar' K200 film offers an excellent combination of properties including:-

- Intrinsic long term heat stability
- Low flammability and extremely low smoke and toxic gas evolution on burning
- Resistance to attack by a wide range of organic and inorganic chemicals and solvents.
- Low water absorption and good hydrolysis resistance at high temperatures and pressures
- Resistance to radiation (X-rays. beta-rays and gamma-rays) is amongst the best of thermoplastic materials.
- Good tear and fatigue resistance
- Retention of good electrical properties over a wide temperature range.

PEEK is an inherently crystalline polymer with a high crystalline melting point of 340°C, but 'Stabar' K200 film has been manufactured in such a way that full crystallinity has not been developed in the film The result is that 'Stabar' K200 is a highly transparent low haze film and has the ability to be thermoformed and embossed at temperatures below 200°C Heat treatment of 'Stabar' K200 film between its melting point and the glass transition temperature of 143°C will induce crystallisation as seen by the onset of opacity, higher rigidity at high temperatures, and improved solvent resistance

'Stabar' K200 film can be adhesion-bonded either to itself or to other substrates, the bond strengths being dependent upon the type of adhesive and the surface preparation

'Stabar' K200 film may be fusion-bonded to itself, to reinforcements and to other substrates by application of heat and pressure.

'Stabar' K200 film can be metallised by vacuum deposition and sputtering techniques, and is compatible with a range of inks and laquers.

ICI Films

POLYPLEX A/S

Kunstharpikser
Teknisk datablad

ALPOLIT UPS 294 V

TYPE
Højreaktiv, tixotrop og for-accelereret orthophthalsyre-polyester.
Lav styrenfordampning.

ANVENDELSE
ALPOLIT UPS 294 V forener stor brudforlængelse med gode mekaniske styrkeegenskaber og høj varmebestandighed.
ALPOLIT UPS 294 V anvendes derfor særligt til møllevinger og tekniske detaljer, hvor disse egenskaber er påkrævet. Tixotropien og god evne til befugtning af glasarmeringen letter lamineringsarbejdet på lodrette flader. Hærdningen sker blot ved tilsætning af peroxid.

SPECIFIKATIONER I FLYDENDE TILSTAND:		
	Styrenindhold	ca. 43%
	Viskositet v. 20°C	250-300 mPa·s
	Densitet v. 20°C	1,10 g/ml
	Syretal	< 20 mg KOH/g
	Lagerbestandighed	4 mdr.
	Geltid v. 20°C *	35-45 min.
	SPI-geltest:	
	Geltime	7,5-8,5 min.
	Curetime	12,0-15,0 min.
	Peak exotherm	110-130°C
EGENSKABER I HÆRDET TILSTAND UDEN ARMERING **:		
	Densitet v. 20°C	1,20 g/ml
	Trækstyrke	65 N/mm²(650 Kp/cm²)
	Bøjestyrke	100 N/mm²(1000 Kp/cm²)
	Elasticitetsmodul	4000 N/mm²(40000 Kp/cm²)
	Brudforlængelse	3,5%
	BARCOL hårdhed	45
	MARTENS værdi	72°C
	HDT (ISO R-75)	100°C
EGENSKABER I HÆRDET TILSTAND ARMERET MED 30% GLASFIBER-MÅTTE **:		
	Trækstyrke	155 N/mm²(1550 Kp/cm²)
	Bøjestyrke	250 N/mm²(2500 Kp/cm²)
	Elasticitetsmodul	7300 N/mm²(73000 Kp/cm²)
	Brudforlængelse	3,1%

* Hærdesystem: 1% MEKP-opl. (50%)
** Efterhærdning 2 timer v. 100°C

For miljø-polyester gælder generelt, at en polyesterrig og glat overflade kan give risiko for nedsat vedhæftningsevne. Ved viderebygning på et laminat skal overfladen vise fiberstruktur, og arealer med meget polyester skal slibes samt rengøres.

Egenskaberne i hærdet tilstand er fremkommet ved laboratorieforsøg, og er givet ud fra vort bedste vidende, som en vejledning til vore kunder, og er uden ansvar for os.

CIBA–GEIGY
Aktieselskab
Lyngbyvej 172 · 2100 Kbhvn. Ø
Tlf. (01) 29 14 22

Teknisk datablad

® ARALDIT LY 5052
HÆRDER HY 5052

Koldt- og varmthærdende lamineringsssystem med lav viskositet uden opløsningsmidler. Til produktion af avancerede fiberforstærkede konstruktioner.

Anvendelsesområder :

Flydele.
Bådebygning.
Sportsartikler.
Reparationer.

Forarbejdningsmetoder :

Injection (vakuum, tryk)
Håndoplægning
Filament vinding
Pressestøbning

Særlige egenskaber :

- fremragende mekaniske. og dynamiske styrker
- godt egnet som matrix-system for alle normalt forekommende forstærkningsfibre
- høj varmefasthed ved efterhærdning
- hurtig og fuldstændig imprægnering af forstærk. ningsmaterialerne
- let at håndtere

Blandingsforhold :

	vægtdele
ARALDIT LY 5052	100 ± 1,0
Hærder HY 5052	38 ± 0,5

Egenskaber

før udhærdning i leveringsformen		
Araldit LY 5052		
leveringsform		klar, flydende
viskositet v/25°C	mPas	1000-1500
volumenvægt v/25°C	g/cm^3	1,16-1,18
Hærder HY 5052		
leveringsform		klar, flydende
viskositet v/25°C	mPas	40-60
volumenvægt v/25°C	g/cm^3	0,93-0,95
Efter blanding af harpiks og hærder		
viskositet v/25°C	mPas	600-700
viskositet v/40°C	mPas	200-250
brugstid (100 g)		
v/23°C	min.	220-260
v/40°C	min.	45-55

SIGRAFIL® Prepreg

Carbonfaser Prepreg Type CE 1007

Vorprodukte	Faser	Carbonfaser nach LN 29.964, Type KC 20		
	Textiles Produkt	Unidirektionale Rovings		
	Harztyp	Epoxidharzsystem		
Eigenschaften	Prepregflächengewicht		g/m²	219 ± 5
	Faserflächengewicht		g/m²	131 ± 3
	Faseranteil		Gew.%	60 ± 2
	Prepregdicke, im Laminat verpreßt		mm	0,125
	Lagerfähigkeit bei – 18 °C		Monate	12
	Lagerfähigkeit bei RT		Monate	2
	Flüchtige Bestandteile		Gew.%	abhängig von der Harzvariante
	Harzfluß		Gew.%	
	Klebkraft		N/cm	
Lieferform	Breite		mm	75, 150, 300
	Länge		m	50, 100, 150
	Kaschierung		ein- oder beidseitig mit Papier	
Verarbeitung	Als Geräte werden Presse oder Autoklav empfohlen Laminate werden bei 120 °C für 2 h gehärtet Höhere Temperaturen verkürzen die Härtedauer			

Verbundwerkstoff-Daten
ermittelt nach LN 29971, WL 5.3231

		Temperatur	
		RT	
Dichte	g/cm³	1,54	
Biegefestigkeit	N/mm²	1800	
E-Modul aus Zug und Biegung	kN/mm²	130	
Zugfestigkeit	N/mm²		
Interlaminare Scherfestigkeit	N/mm²	80 – 90	
Interlaminare Scherfestigkeit nach 1000 h bei 150 °C	N/mm²		
Glastemperatur Tg, trocken	°C		
Fasergehalt	Vol.%	60	
Dauereinsatztemperatur	ca. 120 °C		

SIGRI

SCANDINAVIAN GLASFIBER

Produktdatablad
RPA38
Datum 1988-07-20
Ersätter 1986-07-01

RPA38

I. Produktbeskrivning

RPA38 är en enpartig s k processroving av E-glas. RPA38 är en mjuk, snabbvätande silanroving som ger mycket god bindning till de flesta typer av plast. Rovingen har mycket jämn fiberspänning och god bandformighet för störningsfri urdragning och är avsedd för lindning och profildragning samt vävning. RPA38 är vit, men rovingspolens ändytor kan ha en svag grågul färgton. Rovingen kan även levereras på hylsa (H).

Rovingen motsvarar fordringarna enligt SS 22 41 38 (ISO 2797).

II. Standardtyper

Produktbeteckning	Garnvikt g/1000 m (tex)
RPA38 20 EC12-300	300
RPA38 20 EC14-410	410
→ RPA38 20 EC12-600	600
RPA38 20 EC13-740	740
RPA38 20 EC14-900	900
RPA38 20 EC17-1200	1200
RPA38 H21 EC17-1200	1200
RPA38 21 EC17-2400	2400
RPA38 21 EC24-2400	2400
RPA38 H21 EC24-2400	2400
RPA38 20 EC24-4800	4800

Glas / Polyester

RPA38 20/9 B
EC 12-600

Alpolit UPS 294V

TORAYCA
QUALITY CARBON FIBRE

TECHNICAL DATA SHEET

DATA SHEET NO. TY-117A June, 1983

FIBRE SPECIFICATION
M40 6,000 FILAMENT

Fibre Specification

TORAYCA fibre properties are measured using an impregnated strand test. Lot average of TORAYCA fibre properties are as listed below.

Property	Unit	Lot Average NOM.	MIN.	MAX.
Tensile Strength	MPa ($kg\cdot f/mm^2$)	2,255 (230)	1,961 (200)	— —
Tensile Modulus	GPa ($10^3 kg\cdot f/mm^2$)	392 (40.0)	368 (37.5)	417 (42.5)
Yield	g/1000m	364	348	380
Density	g/cm^3	1.81	1.77	1.85

Quality Control Data

Above properties are available as "TORAYCA CARBON FIBRE CERTIFICATION" on each shipment.

Quality Assurance Testing

Sampling procedure and test methods to be used in certifying performance to the requirements of this specification are described in TECHNICAL DATA SHEET NO. TY-020A and TY-030A.

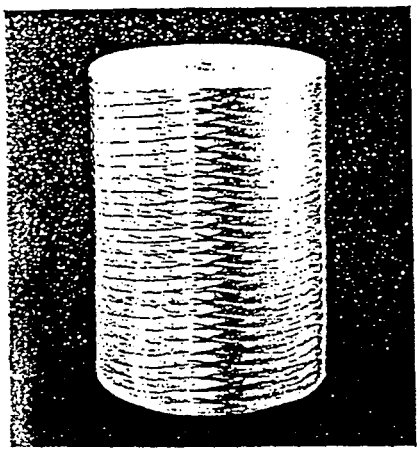
Physical Properties

The physical property characteristics are as listed below.

Property	Unit	Value
Number of Filaments	—	6,000
Filament Diameter	μ	6.5
Cross Sectional Area of Strand	mm^2	0.20
Twist	turn/m	15 (twisted type) 0 (untwisted type)
Carbon Content	%	100
Specific Heat	$cal/g^\circ C$	0.17
Volume Resistivity	$\Omega\cdot cm$	0.8×10^{-3}

Note:
Twisted Yarn : M40 6000
Untwisted Yarn : M40B 6000

Silenka
glass fibre



ASSEMBLED

ROVINGS FOR FILAMENT WINDING AND PULTRUSION

A rapid and complete wet out of the glass fibres is essential for a roving for filament winding and pultrusion.

Roving for filament winding is often used in the production of pipes and tanks, or, in other words, an end use area indicated by 'anti-corrosion'.

Of course the resin largely determines the degree of protection against corrosive influences and the glass fibre must be seen as reinforcement of the resin. However the way the glass fibres behave in the resin helps in many cases to determine the anti-corrosive properties of the product.

Air entrapment must be avoided as much as possible and the filaments must be completely surrounded by resin.

This is even more important with pultrusion because this technique produces for instance rods which are used as electrical insulators. Even minuscule air pockets have great influence on the dielectric breakdown of the glass fibre reinforced plastic.

In view of the generally short distance between the impregnating bath and mandrel or in the case of pultrusion between impreganating bath and heated forming die through which glass fibre and resin are pulled, not only a complete but also an extremely rapid wet out is necessary.

As opposed to rovings which are chopped the filament diameter for rovings for filament winding and pultrusion is relatively unimportant.

The glass fibres are brought into the resin in continuous form and are usually loaded under stress. The total cross section is essential.

ROVING 084

Silenka roving 084 is a multi-end roving. The special silane finish facilitates rapid and complete impregnation and a good bond between fibre and resin.

Silenka has many years of experience with products for filament winding and pultrusion. This experience together with new insights and new raw materials for finishes was used for the development of Roving 084.

The composition of the finish is such that the roving can be successfully used for reinforcement of most of the resins used in the production of pipes and tanks:

- unsaturated polyester resins
- epoxy resin
- vinyl ester resin
- polyurethane resin

Pultruded rods processed with Silenka Roving 084 not only have very good mechanical properties but also the electrical insulation properties are excellent.

For this reason Roving 084 is used in high voltage line insulator rods, transformers, choke-coils and many other sophisticated products.

OTHER TEXES AVAILABLE
300 | 900 | 1800 .

Silenka bv P.O. Box 50 • 9600 AB Hoogezand • The Netherlands

Bibliographic Data Sheet **Risø-R-905(EN)**

Title and author

Materials for Cryogenic Storage of Hydrogen and Natural Gas
Allan Schrøder Pedersen

ISBN 87-550-2192-1 ISSN 0106-2840

Project/contract No ENS-1443/94-0003

Department Date

Materials Department February 1997

Pages	Tables	Illustrations	References
36	2	23	2

Abstract

Experiments have been carried out to describe the properties of selected plastic composites in relation to their use in liquid gas containers.

Gas diffusion into the materials was measured by gravimetry. No uptake of gas was found at 77 K for the measured materials. For the majority of materials no uptake could be detected even at room temperature. In one case, PEEK, an uptake was measured at room temperature, but the rate was so low that it was concluded not to represent a hazard.

Mechanical properties of 7 composite samples were measured by tensile testing and simultaneous recording of the accumulated acoustic emission caused by crack formation. For one material the acoustic emission indicated crack formation at relatively low stress. The rest of the samples only showed negligible acoustic emission up to 150 MPa, which is considered to be sufficient for application in a liquid gas container.

In conclusion the work indicates, that plastic composites are suitable for low temperature gas containers.

Descriptors INIS/EDB
Acoustic Emission Testing, Containers, Cracks, Diffusion, Fibers, Hydrogen, Liquefied Gases, Mechanical Properties, Natural Gas, Organic Polymers, Storage Facilities, Temperature Range 0065-0273 K

Available on request from Information Service Department, Risø National Laboratory, (Afdelingen for Informationsservice, Risø National Laboratory), P.O.Box 49,
DK-4000 Roskilde, Denmark.
Telephone +45 46 77 46 77, ext. 4004/4005
Telex 43 116, Telefax +45 4675 5627